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Influence of Urbanization and Industries on the Pollution of Rivers of Gjilan Municipality, Kosovo

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Abstract

Gjilan (42°28′08″ V, 21°27′48″ L) is one of the seven largest cities in Kosovo. Throughout the city flow three rivers: Mirusha and Stanishor which mix and discharge into the largest river called Morava. The reason for the research of these rivers is the extreme pollution resulting from the discharge of industrial waters. Analysis of these rivers shows that they are extremely polluted and some physicochemical parameters are not in accordance with the regulations of the European Union (EU) and the World Health Organization (WHO). Parameters analysed are: pH, CW, NTU, DO, COD, BOD5, A-HCl, HCO_3, GH, CS, Cl^-, Cl_2, Ca^{2+}, Mg^{2+}, NO_2^-, NO_3^-, PO_4^{3-}, and NH_3^-.

Keywords

Rivers, industries, extreme pollution, physicochemical parameters, EU, WHO

1 Introduction

The increment in the world's population and the overwhelming industrial development has made water supply a problem on our planet, thus imposing the need for rapid long-term solutions.[1] Today it is acknowledged that environmental protection should be given the highest priority, because the preservation of the continuity of life depends on it. Our knowledge of the environment is increasing constantly, and we now have enough knowledge about the chemical composition of our planet and developing processes. Resources (natural resources) of land are finite, and the exploitation and contamination of its systems on the regenerative possibilities have important implications for life on it.[2] Water pollution from chemical substances can be divided into two groups: inorganic and organic chemical contamination. Inorganic pollutants include: nitrates, nitrites, sulphates, heavy metals, *etc.* Organic pollutants include oil and its derivatives, such as soaps, detergents, textile industry effluents, paper, phenols, radioactive materials, *etc.*[3] Water is a substance with a number of unique properties of great environmental significance. Water quality standards have legislative support and specify the characteristics for water.[4] In order to prove the quality of these rivers, physicochemical parameters were determined by international methods, as presented in the Table 1.

Alkalinity refers to the capability of water to neutralize acid. This is really an expression of buffering capacity. A buffer is a solution to which an acid can be added without changing the concentration of available H^+ ions (without changing the pH) appreciably. Ammonia appears in different contrition in groundwater, surface water, and wastewater. Its appearance in water and in loess is described as a result of the reduction of nitrogen-containing organic matter, deamination of amines, hydrolysis of corn, *etc.*, where all nitrogen appears as NH_4 or NH_3. Orthophosphates (PO_4^{3-}) are soluble salts of phosphoric acid, which dissolve into tinctures in humans, depending on the pH of the environment. Orthophosphates are used as artificial fertilizers in land, which dissolve and flow into surface water.

Chlorides are anions distributed in surface water and wastewater, while their concentration in natural water varies greatly. The chloride ion (Cl^-) with appropriate oxidizing agents has a higher redox potential than chlorine (Cl_2).[5] The characteristic of primary importance in many water systems is the amount of *dissolved oxygen* (DO), which can be quickly expended by the oxidation of organic material. In addition, the oxygen in water can even be consumed by bio-oxidation of dissolved ammonia or chemical iron oxidation Fe^{2+} or SO_3^{2-}.

Nitrites, which are produced by nitrogen oxidation, are polyanion monovalent (NO_3^-). Most of the metal nitrates are soluble in water and appear in very small quantities. They appear in trace amounts in surface and groundwater. The main source of nitrite ions (NO_2^-) in unpolluted surface water is the process of mineralization of organic matter and nitrification from bacteria.[6] The most important parameters for determination of organic pollution, also applied in wastewater and surface water, is 5-day biochemical oxygen demand (BOD5). BOD is not a measurement of a specific pollutant, but the measurement of the amount of oxygen required by aerobic bacteria and other microorganisms for the decomposition of organic matter. Most of all, organic substances, which are biologically difficult to oxidize, can be chemically oxidized. Thus, chemical oxygen demand (COD) is generally higher than BOD.[7] Water containing a larger amount of dissolved salts of alkaline earth metals is called strong water as opposed to mild water in which the amount of these salts is small.[1] The calcium ions are very important only for euchroites. The quantity of calcium in organisms is used only for support and to build structures such as teeth. Magnesium ions are ions dominated by 2^+ in the cytoplasm and the only ions

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found free, unrelated to the minimum levels.[8] Determination of these physicochemical parameters in water allows us to determine the pollution from industry, urban sewage, farms, *etc*. Extreme pollution is an expression of biological pollution from industry when BOD and COD exceeds the allowed values prescribed by European Union (EU) and World Health Organization (WHO) standards.

In ancient times, water pollution was low, perhaps because of smaller population. The industrial revolution and large population growth have led to serious environmental pollution.[9]

Table 1 – Permissibility criteria for physicochemical parameters according to WHO (ref.[10], p. 35)
Tablica 1 – Dopušteni kriteriji za fizikalno-kemijske parametre prema SZO-u (lit.[10], str. 35)

Parameters Parametri	Symbol / unit Simbol / jedinica	WHO SZO
pH	pH	6.8–8.5
conductivity of water vodljivost vode	CW / S m^{-1}	<50
nephelometric turbidity unit nefelometarska jedinica mutnoće	NTU	10
dissolved oxygen otopljeni kisik	DO / mg l^{-1}	>5
chemical oxygen demand kemijska potrošnja kisika	COD / mg l^{-1}	10
5-day biochemical oxygen demand petodnevna biokemijska potrošnja kisika	BOD5 / mg l^{-1}	<3
alkalinity akalnost	A-HCl / mg l^{-1}	10.5
bicarbonates bikarbonati	HCO_3^- / mg l^{-1}	630
general hardness ukupna tvrdoća	GH / °dH	30
calcium kalcij	Ca^{2+} / mg l^{-1}	<200
magnesium magnezij	Mg^{2+} / mg l^{-1}	<50
chlorides kloridi	Cl^- / mg l^{-1}	<200
chlorine klor	Cl_2 / mg l^{-1}	0.2–0.5
nitrites nitriti	NO_2^- / mg l^{-1}	0.6
nitrates nitrati	NO_3^- / mg l^{-1}	10
phosphates fosfati	PO_4^{3-} / mg l^{-1}	0.2
ammonia amonijak	NH_3^- / mg l^{-1}	0.05

2 Experimental

2.1 Chemicals

Ethylenediaminetetraacetic acid (EDTA), Nitri Ver 3 reagent (USA), Nitra Ver 5 reagent (USA), Ammonia Salicylate reagent (USA), Ammonia Cyanurate reagent (USA), Phos Ver 3 reagent (USA), DPD Total Chlorine reagent (USA), $AgNO_3$ (c = 0.01 mol l^{-1}), HCl (c = 0.01 mol l^{-1}), buffer, indicator (black erythromycin), indicator (methylorange), indicator (phenolphthalein), indicator (black murexide), NaOH (c = 2 mol l^{-1}), methylene chloride, $K_2Cr_2O_7$, H_2SO_4 98 %, glucose.

2.2 Physicochemical parameters and methods of analysis

Absorption spectrometry in the ultraviolet and visible region is based on the electromagnetic radiation absorption of molecules in the UV spectra of 160–400 nm and VIS 400–780 nm range. UV-VIS radiation absorption causes the excitation of the electrons of chemical bonds by passing the molecules to higher energy levels.[11] The absorption of UV-VIS radiation from complex molecules and inorganic salts of transitional metals, as well as of lanthanides and actinides, causes the molecule to move from its basal to its excited state.[12] The Hach Model DR/2010 Spectrophotometer is a microprocessor-controlled single-beam instrument for colorimetric testing in the laboratory or in the field. The instrument is precalibrated for over 120 different colorimetric measurements and allows convenient calibrations for user-entered and future Hach methods.[13]

The pH, conductivity of water (CW), and dissolved oxygen (DO) were determined at the sampling points using a portable multiparameter analyser. Other chemical parameters were determined according to the standard analytical methods for the examination of water and wastewater according to the WHO and EU standards (see Table 1). The value of pH was determined using a portable multiparameter analyser, WTW 3010. *Conductivity of water* (CW), also known as *specific conductivity*, represents the ability of water to convey electricity, and is related to the concentration of ionized substances in water.[2] CW was determined with WTW Cond 3110, DO was determined with WTW Oxi 315i, and NTU was determined with 2100N ISC Turbidimeter (ISO Method 7027).

The *chemical oxygen demand* (COD) represents the amount of oxygen from organic matter, which is subjected to oxidation by any strong oxidizing agent.[6] COD was determined in the instrument Photometer Winlab on λ = 610 nm. The standard was prepared with 3 ml of glucose, 2 ml of $K_2Cr_2O_7$, and 5 ml of H_2SO_4. Blank was prepared with 3 ml of distilled water, 2 ml of $K_2Cr_2O_7$, and 5 ml of H_2SO_4, and sample with 3 ml of contaminated water, 2 ml $K_2Cr_2O_7$, and 5 ml H_2SO_4 in the cuvette. Before being placed in the photometer, they were up to 150 °C for 2 h.

As a result of the oxidation of organic matter by microorganisms, the biochemical oxygen demand in the well-preserved water sample decreases in time. Empirically, BOD5 is the amount of the consumed oxygen needed to oxidize the organic matter into the sample. The most commonly used test, BOD5, is based on a 5-day incubation of sample at 20 °C ± 1 °C. The tool used was "OxiTop", which was filled with water up to 250 ml.

Nitrite (NO_2^-) concentration was determined using Nitri Ver 3 reagent (Nitrite Test 2 – 150 mg l^{-1}, Method 8153), and the absorbance level was then measured using a spectrophotometer (HACH DR 900, USA). Nitrate (NO_3^-) concentration was determined using Nitra Ver 5 reagent (Nitrate Test 0–30 mg l^{-1}, Method 8039), and the absorbance level was then measured using a spectrophotometer (HACH DR/2010, USA) at $\lambda = 500$ nm. Nitrogen ammonia (NH_3^-) concentration was determined using ammonia salicylate reagent in first step, and then using ammonia cyanurate reagent (Nitrogen Ammonia Test 0–0.50 mg l^{-1}, Method 8155) in second step. The absorbance level was then measured using a spectrophotometer (HACH DR/2010, USA) at $\lambda = 655$ nm.

Phosphate (PO_4^{-3}) concentration was determined using Phos Ver 3 reagent (Phosfate Test 0–2.50 mg l^{-1}, Method 8048), and the absorbance level was then measured using a spectrophotometer (HACH DR/2010, USA) at $\lambda = 890$ nm.

For the determination of chlorine (Cl_2), DPD Total Chlorine reagent (Chlorine Test 0.02–2 mg l^{-1}, Method 8167) was used. The absorbance level did not exist and was then measured using a Pocket Colorimeter II (HACH, USA).

The determination of chlorides was carried out in an Erlenmeyer flask containing 100 ml of water sample (adjust pH 7–10 if necessary). With the addition of 1 ml of K_2CrO_4, the sample turned yellowish. Titration was done with silver nitrate ($AgNO_3$ ($c = 0.01$ mol l^{-1})) and it stopped at the moment when the solution gets light red.[1] The value of the chlorides in the sample was calculated according to Eq. (1):

$$\mathrm{Cl^-/mg\ l^{-1}} = 35.453 \cdot c \cdot \frac{(V_1 - V_2)}{V_s}\,, \qquad (1)$$

where V_1 is the volume of the titre for the sample (ml), V_2 is the volume of the titre for blind sample (ml), c is molarity $AgNO_3$ ($c = 0.01$ mol l^{-1}), and V_s is the volume of the sample used (100 ml in our case).

Water sample alkalinity (*A*) is the measurement of its capacity to neutralize the acids. Water accumulation is mainly due to weak acid salts. In 100 ml of the analysed sample, 4 drops of phenolphthalein were added. If the 100 ml solution became purple, that meant the water contained bases due to pH above 8.3, and if the solution did not turn purple, 2 to 3 drops of methylorange were added, which turned the solution yellow. The solution was then titrated with HCl ($c = 0.01$ mol l^{-1}) until it turned orange, and the amount of titre used was recorded.[1]

Water hardness or general hardness (GH) was achieved by pouring 100 ml of sample into a 250-ml flask, adding 2–5 ml of buffer and indicator (black erythromycin) in very small quantities. Following the addition of the indicator, the solution became red or light red, and the titration was done with complexon III or EDTA ($c = 0.01$ mol l^{-1}) until the solution changed its colour to intensive blue.[1] The calculation was made based on Eq. (2):

$$\mathrm{GH/mg\ l^{-1}} = \frac{V_{\mathrm{EDTA}} \cdot c_{\mathrm{EDTA}} \cdot 56 \cdot 1000}{V}\,, \qquad (2)$$

where V_{EDTA} is the titration volume (ml) with ethylenediaminetetraacetic acid, c_{EDTA} is the concentration of EDTA ($c = 0.01$ mol l^{-1}), and V_s is the volume of the sample used.

Carbonate strength (CS) is defined as the alkalinity to methylorange. A volume of 100 ml water sample was transferred to 500-ml Erlenmeyer flask and 2–3 drops of methylene chloride were added. The titration was performed with standard solution HCl ($c = 0.01$ mol l^{-1}) until the colour changed to orange. The analysis results were calculated in German degrees (°dH) water hardness scale according to Eq. (3)

$$\mathrm{CS/°dH} = 2.8 \cdot V_{\mathrm{HCL}} \cdot c_{\mathrm{HCL}}\,, \qquad (3)$$

where 2.8 value is the constant, V_{HCL} is consumed volume of HCl, and c_{HCL} is the concentration of HCl ($c = 0.01$ mol l^{-1}).

First, we get 100 ml of water, add 5 ml of buffer solution (in this case NaOH ($c = 2$ mol l^{-1})) and a black murexide indicator (black murexide is prepared from ammonia purities mixed with NaCL ($c = 0.01$ mol l^{-1}), and titrated with EDTA ($c = 0.01$ mol l^{-1}) to change the colour from red to purple. The titration should be carried out for 5 min after the addition of NaOH.[1] The determination of Ca^{2+} was calculated by the following Eq. (4):

$$\mathrm{Ca^{2+}/mg\ l^{-1}} = \frac{V_{\mathrm{EDTA}} \cdot c_{\mathrm{EDTA}} \cdot 56 \cdot 1000}{V_s}\,, \qquad (4)$$

where V_{EDTA} is the volume (ml) of the titre with ethylenediaminetetraacetic acid, c_{EDTA} is the concentration of EDTA ($c = 0.01$ mol l^{-1}), and V_s is the volume of the sample used.

Determination of Mg^{2+} was calculated with the following Eq. (5):

$$\mathrm{Mg^{2+}/mg\ l^{-1}} = \frac{\mathrm{GH/°dH} - \mathrm{Ca^{2+}/mg\ l^{-1}}}{10} \cdot 7.19\,. \qquad (5)$$

3 Results and discussion

3.1 Location of the analysed samples

Mirusha and Stanishor rivers are surface waters, characterized by low volumes during the summer, while during the winter season, the waters of these rivers are more voluminous. These two rivers flow into the rapid-flowing river called "Morava e Binçës". These rivers are highly polluted because sewage and industrial waters are discharged into them (Fig. 1). The source of the Mirusha River is in the village of Koretisht, and is called "holy water" by the inhabitants of this village, but the problem is that during its flow, it collects various impurities and sewage. The Stanishor River is also polluted, while its source is clean. The river rises in the suburbs of Gjilan and takes the name Stanishor accord-

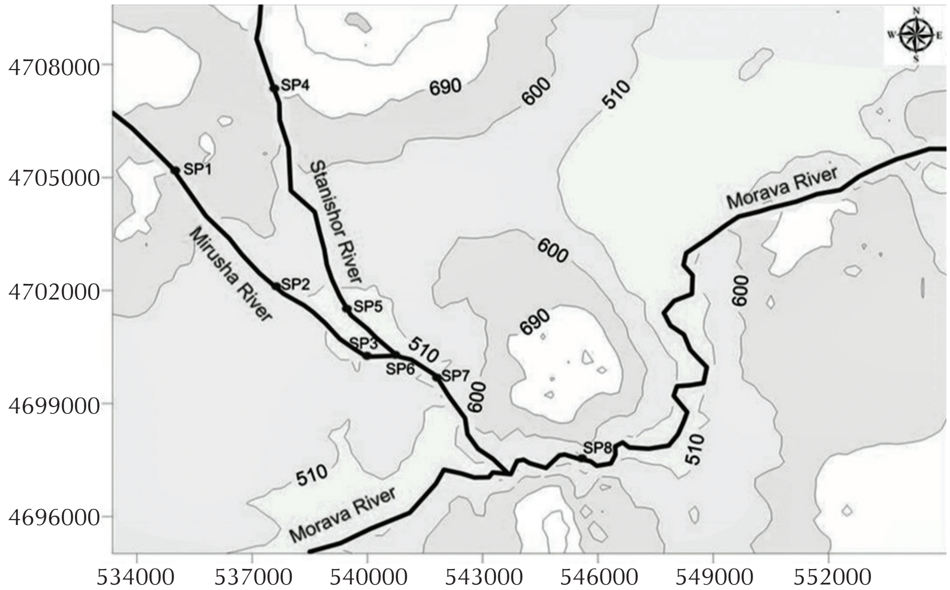

Fig. 1 – Monitoring network of the river research area (ref.[10], p. 21)
Slika 1 – Mreža za praćenje područja istraživanja rijeka (lit.[10], str. 21)

ing to the village from which it springs. Morava e Binçës belongs to the Black Sea basin. It joins the Western Morava, which merges and flows into the Danube and then into the Black Sea. The description of the sampling locations of the Mirusha, Stanishor, and Morava rivers is very important in explaining the network of monitoring the physical and chemical parameters of these rivers. Sample SP_1 belongs to the Mirusha River resource, sample SP_2 was taken after the river passes Koretisht village, while sample SP_3 was taken after the river passes the town of Gjilan. Sample SP_4 was taken from the Stanishor River basin, and sample SP_5 was taken after passing the Gjilan City. Sample SP_6 was taken at the merging point of the two rivers. Sample SP_7 was taken further downstream from sample SP_6, and sample SP_8 belongs to the Morava River.

3.2 Results of pH determination

These contaminated rivers have pH varying between 7.2 and 7.39, which does not express concern. In SP_1, pH was 7.2, but as the water flows and passes through the village, the pH of SP_2 increased to 7.28. In addition, the pH of SP_3 was 7.33. Again, pH increased to 7.33. SP_4 was taken from the Stanishor River, which was pH 7.38, but at the entrance to the city, after passing through the village and the city, pH increased to 7.39 in sample SP_5, while in SP_6, which was taken where the two rivers merge, the pH reduced to 7.37. In SP_7, the pH was reduced to 7.25, while in SP_8, of the Morava River the pH rose again to 7.3 (Table 2). The pH of these water samples are in accordance with WHO and EU regulations (Table 1).

3.3 Results for the conductivity of water (CW)

Conductivity of water (CW) from the source of the Mirusha River to the exit of the city increased from 14.9 to 28.5 $S\,m^{-1}$. In sample SP_1, CW was 14.9 $S\,m^{-1}$, in SP_2 at the exit of the village CW increased to 24.3 $S\,m^{-1}$, while in SP_3 CW was 28.5 $S\,m^{-1}$ (Fig. 1). Thus, an increase in electrical conductivity of the water is obvious. On the other hand, in the source of the Stanishor stream SP_4, CW was 31.7, while in SP_5 the CW dropped to 27.3 $S\,m^{-1}$, but at the merging point of the two rivers at SP_6 the value of CW was 24.8 $S\,m^{-1}$, which was lower in comparison to samples SP_3 and SP_5. CW value of sample SP_7 was 27.5 $S\,m^{-1}$, so we see it rising, while in Morava River the CW value in sample SP_8 was 24.1 $S\,m^{-1}$, which is lower compared to SP_2, SP_3, SP_4, SP_5, SP_6, and SP_7. CW values in these rivers are in accordance with EU and WHO regulations (Table 1).

3.4 Results for nephelometric turbidity unit (NTU)

Nephelometric turbidity unit (NTU) is a measure of relative purity or water turbidity. Turbidity is a feature of absorbing light or distributing it from suspended water.[14]

In the SP_1 sample, the value of NTU was 0.295 at the Mirusha River site and within the allowed criteria, but the obtained value of NTU in SP_2 sample was 42.2, which is not in accordance with EU and WHO regulations (Table 1). The sample SP_3 taken out of the city had NTU value of 57.8, so while passing through the village and the city, NTU value increases more and more due to uncontrolled urban and industrial wastewater. In sample SP_4 or in the Stanishor River basin, the NTU value was 0.626, but that river in the city or sample SP_5 had NTU value 53.6. NTU value at the merging point of the two rivers, sample SP_6, was 14.5, thus, a decrease in turbulence is obvious. In sample SP_7, NTU was 66.1, and the Morava River SP_8 sample NTU value was 27.5 (Fig. 1).

(i) In first group of samples SP_1 and SP_4, the NTU values are in the accordance with the EU and WHO regulations.

(ii) In the second set of samples – SP_2, SP_3, SP_5, SP_6, SP_7, and SP_8, NTU values are not in accordance with the EU and WHO regulations.

3.5 Results for dissolved oxygen (DO)

Dissolved oxygen (DO) is a very important parameter for biotin. A too low amount of oxygen in water suggests that the water sample taken as in our case may exhibit a very high degree of pollution due to the very high presence of microorganisms. In the SP_1 sample taken at the Mirusha River reservoir, DO was 4.67 mg l^{-1} indicating that it is below the EU and WHO allowed value >5 mg l^{-1}. In the sample SP_2 at the exit of the Koretisht village, DO value was 1.18 mg l^{-1}, suggesting a significant decrease in DO. In the SP_3 sample at the exit of the Mirusha River from Gjilan, DO value was 0.61 mg l^{-1}. Comparison of SP_1 and SP_3 dissolved oxygen (DO) samples revealed a drop to 4.06 mg l^{-1}, and this decline is due to the microorganisms that need oxygen to perform their biological and chemical activities. In the SP_4 sample at the Stanishor River basin, DO value was 4.53 mg l^{-1} indicating that it is below the allowed value, while in the SP_5 sample at the exit of the city of Gjilan, DO value was 0.6 mg l^{-1}. Therefore, if we compare DO from SP_1 and SP_5, the value of DO decreased to 3.93 mg l^{-1}. At the merging point of the rivers Mirusha and Stanishor in sample SP_6, DO value was 1.32 mg l^{-1}. In sample SP_7 (Fig. 1), DO value was 3.36 mg l^{-1}, whereas in sample SP_8 of Morava River, DO was 0.32 mg l^{-1}. The highest and the lowest values in the mentioned locations are divided into two groups:

(i) The first group in the SP_1 and SP_4 samples are not in accordance with the EU and WHO regulations (Table 2).

(ii) The second SP_2, SP_3, SP_4, SP_5, SP_6, SP_7 and SP_8 sampling group is not in accordance with the EU and WHO regulations (Tables 1 and 2).

Table 2 – Physicochemical parameters of the Stanishor, Mirusha and Morava rivers (ref.[6], p. 35)
Tablica 2 – Fizikalno-kemijski parametri rijeka Stanishor, Mirusha i Morava (lit.[6], str. 35)

	Samples Uzorci							
	SP_1	SP_2	SP_3	SP_4	SP_5	SP_6	SP_7	SP_8
°C	9	28	24	11	27	23	22.5	23.4
odour	No	Yes	Yes	No	Yes	Yes	Yes	Yes
pH	7.2	7.28	7.33	7.38	7.39	7.37	7.25	7.3
$CW/\text{S m}^{-1}$	14.9	24.3	28.5	31.7	27.3	24.8	27.5	24.1
NTU	0.295	42.2	57.8	0.626	53.6	14.5	66.1	27.5
$DO/\text{mg l}^{-1}$	4.67	1.18	0.61	4.53	0.6	1.32	3.36	0.32
$COD/\text{mg l}^{-1}$	0.12	3.36	1.7	4.94	0.13	3.1	2.7	1.34
$BOD_5/\text{mg l}^{-1}$	0	0.9	0.8	0	0.6	0.6	0	12
	0	13	11	0	10	14	0.1	19
	0	17	15	0	13	16	0.4	25
	0	19	17	0	15	20	0.3	27
	0	20	18	0	17	21	0.2	29
$\text{A-HCl}/\text{mg l}^{-1}$	6.1	6.8	6.7	5.5	7	7.5	7.8	5.6
$HCO_3^-/\text{mg l}^{-1}$	372.1	414.8	408.7	335.5	427	457.5	475.8	341.6
$GH/{}^\circ\text{dH}$	19.3	17.41	17.92	19.48	18.42	20.16	21	15.28
$Ca^{2+}/\text{mg l}^{-1}$	61.7	126.2	129.05	122.88	140.28	140.8	140.2	102
$Mg^{2+}/\text{mg l}^{-1}$	56.7	20.6	21.6	31.02	18.9	26.4	30.07	21.9
$CS/{}^\circ\text{dH}$	17.08	19.04	18.7	15.4	19.6	21	21.8	15.6
$Cl^-/\text{mg l}^{-1}$	12.3	72	68	29.9	51.9	52.2	73.9	36
$Cl_2/\text{mg l}^{-1}$	0	0.21	0.26	0	0.01	0.07	0.39	0.19
$NO_2^-/\text{mg l}^{-1}$	1	16	11	4	13	12	2	13
$NO_3^-/\text{mg l}^{-1}$	2	6	7	2	4.4	6	6.3	5.6
$PO_4^{-3}/\text{mg l}^{-1}$	0.35	÷	÷	0.33	÷	÷	÷	÷
$NH_3^-/\text{mg l}^{-1}$	0.09	÷	÷	0.03	÷	÷	÷	÷

(÷) immeasurable by spectrophotometer
(÷) znak označava da spektrofotometar ne može analizirati vrijednost tog uzorka jer je izvan mjerne kontrole instrumenta

3.6 Results for chemical oxygen demand (COD)

Chemical oxygen demand (COD) as a chemical parameter indicates in some way whether a sample is chemically contaminated or not. In our case, during the COD research on rivers (Fig. 1), there is no chemical contamination based on the results obtained in the laboratory. In the SP_1 sample, COD value was 0.12 $mg\,l^{-1}$, but at the exit of the village, the COD in the SP_2 sample was 3.36 $mg\,l^{-1}$, so there was a rapid increase in COD, while in SP_3 sample at the exit of the city, COD value was 1.7 $mg\,l^{-1}$ (Table 2). In the Stanishor River basin, COD was higher than in the samples contaminated with water, and the COD value in the SP_4 sample reached 4.94 $mg\,l^{-1}$. In the SP_5 samples, COD was 0.13 $mg\,l^{-1}$, while in the SP_6 sample, the amount of COD was 3.1 $mg\,l^{-1}$. The COD of sample SP_7 was 2.7 $mg\,l^{-1}$ and this sample was taken from a greater distance compared to sample SP_6. Sample SP_8 was taken in the Morava River, in which COD value was 1.34 $mg\,l^{-1}$. Therefore, according to all mentioned results, the highest COD value was found in sample SP_4 of the Stanishor River, but COD as a chemical parameter was higher in the Mirusha River than in the Stanishor River. In conclusion, all of these values are not in accordance with EU and WHO regulations (Table 1).

3.7 Results for 5-day biochemical oxygen demand (BOD5)

Biochemical oxygen demand (BOD) is a very important parameter to determine the biological level of water pollution. BOD5 in sample SP_1 was 0 $mg\,l^{-1}$, but during the flow of water from the Mirusha River site to the village exit, the amount of BOD5 in sample SP_2 was as high as 20 $mg\,l^{-1}$. In sample SP_3, BOD5 was 18 $mg\,l^{-1}$, so from SP_2 to SP_3 sampling site, the amount of BOD5 reduced by 2 $mg\,l^{-1}$. BOD5 in sample SP_4, which was the source of the Stanishor River, was 0 $mg\,l^{-1}$, while in sample SP_5 the amount of BOD5 was 17 $mg\,l^{-1}$, a very large increase compared to the BOD5 of the Stanishor River basin. In sample SP_6, BOD5 was 21 $mg\,l^{-1}$ (Table 2). BOD5 in sample SP_7 was 0.2 $mg\,l^{-1}$. This is a very large drop in the biochemical consumption of oxygen, but in the Morava River, unfortunately, the quantity of BOD5 was 29 $mg\,l^{-1}$ and the value was higher than all other analysed samples. The lower and higher values of BOD5 are divided into two groups:

(i) In the first group with the locations SP_1, SP_4 and SP_7 (Fig. 1), BOD5 values range from 0 to 0.2 $mg\,l^{-1}$, which is in accordance with EU and WHO regulations.

(ii) In the second group with SP_2, SP_3, SP_5, SP_6 and SP_8 locations, BOD5 values range from 18 to 29 $mg\,l^{-1}$, indicating extreme contamination because >10 $mg\,l^{-1}$ was calculated as extreme contamination. These values are not in accordance with EU and WHO regulations (Tables 1 and 2).

3.8 Results for alkalinity

All samples from SP_1 to SP_8 had HCl values from 5.5 to 7.8 ml (Table 2), so there was no need for analysis of this parameter, because all the values were in accordance with EU and WHO regulations (Table 1).

3.9 Results for bicarbonates HCO_3^-

During the determination of HCO_3^-, it can be seen that from one sampling point to another, its value had increased. In sample SP_1, HCO_3^- value was 372.1 $mg\,l^{-1}$, while in sample SP_2, HCO_3^- was 414.8 $mg\,l^{-1}$. In sample SP_3, there was a decrease in HCO_3^- value (408.7 $mg\,l^{-1}$) compared to the SP_1 and SP_2 samples. At the SP_4 site, HCO_3^- was 335.5 $mg\,l^{-1}$, but at the exit of the city where sample SP_5 was taken, HCO_3^- value was 427 $mg\,l^{-1}$, *i.e.*, a higher HCO_3^- value compared to sample SP_4, which was taken at the Stanishor River basin. The amount of HCO_3^- in sample SP_6 was 457.5 $mg\,l^{-1}$, while sample SP_7 showed an increase in HCO_3^- up to 475.8 $mg\,l^{-1}$. Morava River possess lower HCO_3^- value compared to all other samples, while only in sample SP_8 the value reached 341.6 $mg\,l^{-11}$ (Table 2). Bicarbonates in all samples from SP_1 to SP_8 are in accordance with EU and WHO regulations (Table 1).

3.9 Results for general hardness and carbon strength

Water containing a large amount of dissolved salts of alkaline earth metals is called strong water as opposed to soft water in which the amount of these salts is low. *General hardness* (GH) in all samples from SP_1 to SP_8 enters the strongest water category, where GH value ranges from 15.28 to 21 °dH. In sample SP_1, the GH value was 19.3 °dH, but this value began to drop in samples SP_2 (17.41 °dH) and SP_3 (17.92 °dH). In sample SP_4, GH value was 19.42 °dH, but was lower in sample SP_5 with a value of 18.42 °dH. The GH in sample SP_6 was 20.16 °dH, and in sample SP_7 it was 21 °dH, which is higher compared to sample SP_5, while in sample SP_8 the GH value decreased to 15.28 °dH. All GH values of the aforementioned samples SP_1–SP_8 (Fig. 1) are not included in the category of very strong water at the German °dH degree. The water of Stanishor River was harder compared to the GH of Mirusha River.

Large amounts of sodium bicarbonate or potassium in water will result in greater carbonate hardness than total strength (GH). *Carbon strength* (CS) values in the analysed samples ranged from 15.4 to 21.8 °dH to SP_1–SP_8 samples (Fig. 1). In sample SP_1, CS value was 17.08 °dH, in sample SP_2, CS value was 19.4 °dH. It can be seen that sodium or potassium bicarbonates are higher in SP_2 than in SP_1, while CS is reduced in sample SP_3 at 18.7 °dH compared to SP_2. The CS value in sample SP_4 at the Stanishor River was 15.4 °dH, but in SP_5 at the exit of the Stanishor River, CS value was 19.6 °dH, thus, the CS increased compared to that of SP_4. In sample SP_6, CS value again increased to 21 °dH compared to SP_3 and SP_5. The CS value of SP_7 was 21.8 °dH, but in SP_8 of the Morava River, CS value was reduced at 15.28 °dH. Finally, CS was the highest in the Stanishor River and the lowest in the Mirusha and Morava Rivers (Table 2). GH and CS values in SP_1–SP_8 samples do not present a risk and are in accordance with EU and WHO regulations (Table 1).

3.10 Results for calcium (Ca^{2+})

Calcium (Ca^{2+}) is a very important parameter for water. In our case, its value ranged from 61.7 to 140.28 mg l^{-1} for SP_1–SP_8 (Fig. 1). In SP_1 of the Mirusha River basin, Ca^{2+} value was 61.7 mg l^{-1}, in SP_2 the value of Ca^{2+} was 126.2 mg l^{-1}, and in SP_3 near the merging point with the Stanishor River, the value of Ca^{2+} was 129.05 mg l^{-1}. In SP_4 at the Stanishor River basin, the amount of Ca^{2+} was 122.88 mg l^{-1}, and in SP_5 the Ca^{2+} value was 140.28 mg l^{-1}, thus, the amount of calcium increased in value from the river source to the interconnection between the two rivers – Mirusha and Stanishor. The Ca^{2+} value in SP_6 was 140.8 mg l^{-1} and, compared to the sample of the Mirusha and Stanishor River after mixing these two rivers, Ca^{2+} value increased. In SP_7, the amount of Ca^{2+} did not change significantly compared to SP_5 and SP_6. In SP_8 of the Morava River, the Ca^{2+} content was 102 mg l^{-1}, so the amount of Ca^{2+} in this river was reduced to 38 mg l^{-1} compared to SP_7 (Table 2). The Ca^{2+} values in this river are in accordance with EU and WHO regulations (Table 1).

3.11 Results for magnesium (Mg^{2+})

Magnesium (Mg^{2+}) ions values in samples SP_1–SP_8 (Fig. 1) were not very high, ranging from 20.6 to 56.7 mg l^{-1}. In SP_1 of the Mirusha River basin, Mg^{2+} value was 56.7 mg l^{-1}, which was higher than that of all other samples analysed in the laboratory. In sample SP_2, Mg^{2+} value decreases (20.6 mg l^{-1}) compared to SP_1. The value of Mg^{2+} in SP_3 was 21.6 mg l^{-1}, which was higher by 1 mg l^{-1} in comparison to SP_2. In SP_4 of the Stanishor River basin, the amount of Mg^{2+} was 31.02 mg l^{-1}, but in SP_5 of the Stanishor River, the amount of Mg^{2+} decreased to 18.9 mg l^{-1}. In SP_6, Mg^{2+} value was 26.4 mg l^{-1}, much lower compared to SP_1 and SP_4 at the Mirusha and Stanishor River basins (Table 2). In SP_7, Mg^{2+} value was 30.07 mg l^{-1}, which was higher than that of SP_6. In SP_8 of Morava River, Mg^{2+} value was 21.9 mg l^{-1}. Mg^{2+} values of the river waters are in accordance with EU and WHO regulations (Table 1).

3.12 Results for chlorides (Cl^-)

During laboratory analysis, chlorides (Cl^-) were 12.3–73.9 mg l^{-1} in SP_1–SP_2 (Fig. 1). In SP_1, Cl^- value was 12.3 mg l^{-1}, and in SP_2 Cl^- was 72 mg l^{-1}. It can be seen that the amount of Cl^- increased in SP_2 by 59.7 mg l^{-1} compared to SP_1. In SP_3, the amount of Cl^- was 68 mg l^{-1}, so there was a decrease in the amount of Cl^- in comparison to SP_2. In SP_4 taken at the Stanishor River basin, Cl^- value was 29.9 mg l^{-1}, so the amount of Cl^- was higher compared to the Mirusha River basin in SP_1 (Table 2). In SP_5, Cl^- value was 51.9 mg l^{-11}, so the value was higher compared to SP_4. The amount of Cl^- in SP_6 that was collected after the merging of the Mirusha and Stanishor rivers, was 52.2 mg l^{-1}, while in SP_7, the amount of Cl^- was 73.9 mg l^{-1} which was higher than that in SP_6, while in the SP_8 sample of the Morava River, the value of Cl^- was 36 mg l^{-1}, which is very low compared to SP_7 (Table 2). The value of Cl^- poses no pollution risk, and is in accordance with the allowed EU and WHO values (Table 1).

3.13 Results for chlorine (Cl_2)

Chloride (Cl_2) was determined at sites where SP_1–SP_8 samples were taken (Fig. 1). Cl_2 was defined because if in these waters Cl_2 exceeds 0.5 mg l^{-1}, the potential to form trihalomethans would be very high. Trihalomethans are very dangerous and are formed by the very high amount of chlorine used in the regional water supply system. Sample SP_1 cannot normally be Cl_2 because it is the source of the Mirusha River that originates from the subsoil. In sample SP_2, the Cl_2 value was 0.21 mg l^{-1}, while in SP_3 the value of Cl_2 increased to 0.26 mg l^{-1} compared to SP_2, and this increase in Cl_2 in sample SP_3 occurred due to the release of domestic waters supplied by the regional water supply. In SP_4, Cl_2 value was 0 mg l^{-1} because it is the source of the Stanishor River that originates from the subsoil. In SP_5, the amount of Cl_2 was very low at 0.01 mg l^{-1}, while in SP_6, where the two rivers meet, the amount of Cl_2 was 0.07 mg l^{-1}. In SP_7, Cl_2 value was 0.39 mg l^{-1}, which is very high compared to SP_6, and SP_6–SP_7 are not at a very large distance. In SP_8 of Morava River, Cl_2 value was 0.19 mg l^{-1}, lower compared to sample SP_7 (Table 2). Cl_2 value in these samples are in accordance with allowed EU and WHO values (Table 1).

3.14 Results for nitrites (NO_2^-)

The laboratory analysis of nitrite (NO_2^-) raised concerns, because high values in all the samples, SP_1– SP_8, were determined. In SP_1 of the Mirusha River basin, NO_2^- value was 1 mg l^{-1}, whereas the EU and WHO standards permit NO_2^- amounts up to 0.6 mg l^{-1} (Table 1). In sample SP_2, NO_2^- value increased to 16 mg l^{-1}, while in SP_3 taken at the exit of the city, NO_2^- value was 11 mg l^{-1}. If we compare NO_2^- values from the Mirusha River basin, the amount of nitrite increased significantly, which is very disturbing (Table 2). In SP_4 taken at the Stanishor River basin, NO_2^- value was 4 mg l^{-1}, which is a very high value from a non-polluted wastewater source, while in SP_5 the NO_2^- value was 13 mg l^{-1}. If we compare the NO_2^- value from the Stanishor River source with sample SP_4 up to peak SP_5, NO_2^- value increased by 9 mg l^{-1}. In SP_6 taken at the intersection of the two rivers (Fig. 1), NO_2^- value was 12 mg l^{-1}, while at a greater distance in SP_7 the nitrite value was 2 mg l^{-1}. In sample SP_7, the nitrites significantly decreased, but still exceeded the permitted regulatory range for this parameter. In sample SP_8 taken from the Morava River, NO_2^- value was 13 mg l^{-1}, so even in this river, the amount of nitrite is high. In conclusion, NO_2^- values in these samples are not in accordance with EU and WHO regulations (Table 1).

3.15 Results for nitrates (NO_3^-)

The laboratory analysis of nitrates (NO_3^-) showed that NO_3^- values ranged from 2 to 7 mg l^{-1} in SP_1–SP_8. NO_3^- value in SP_1 was 2 mg l^{-1}, while in SP_2 , the NO_3^- value was 6 mg l^{-1} , which shows an increase in the amount of nitrate compared to SP_1 at the Mirusha River source. In SP_3, nitrates were 7 mg l^{-1}. Compared to SP_2, the NO_3^- value increased by 1 mg l^{-1} in SP_3. In SP_4 of the Mirusha

River basin, the nitrate value was 2 mg l^{-1}, whereas (Table 2) NO$_3^-$ value in SP$_5$ was 4.4 mg l^{-1}, so in SP$_5$ the nitrate value increased to 2.2 mg l^{-1} compared to SP$_4$. In SP$_6$ (Fig. 1), NO$_3^-$ value was 6 mg l^{-1}, so it can be seen that after merging of the Mirusha and Stanishor rivers, the nitrate values increased, while in SP$_7$ the value of NO$_3^-$ again rose to 6.3 mg l^{-1}. In SP$_8$, the NO$_3^-$ value was 5.6 mg l^{-1}, which was less than that of SP$_7$ (Table 2). The NO$_3^-$ values are in accordance with EU and WHO regulations (Table 1), and present no concern.

3.16 Results for phosphates (PO$_4^{3-}$)

During spectrophotometric analysis of phosphate PO$_4^{3-}$ in the laboratory, as referred to in method 8048, the maximum measuring range of the instrument with this method is 2.5 mg l^{-1}. In SP$_1$ of the Mirusha River basin, PO$_4^{3-}$ value was 0.35 mg l^{-1}, whereas in SP$_2$, the PO$_4^{3-}$ value was outside the instrument's measuring range, *i.e.* it was higher than 2.5 mg l^{-1}, and in SP$_3$ it was impossible for the spectrophotometer to give a value of PO$_4^{3-}$ because the value was outside the measuring range. In SP$_4$ taken from the Stanishor River basin, the value of PO$_4^{3-}$ was 0.33 mg l^{-1}, while in SP$_5$, SP$_6$, SP$_7$, and SP$_8$, the values of phosphates (PO$_4^{3-}$) were immeasurable as mentioned above. The phosphate was divided into two groups of samples due to the high pollution present in these rivers (Fig. 1):

(i) The first group of samples that included SP$_1$ and SP$_3$ taken from the Mirusha and Stanishor river basins are not in accordance with EU and WHO regulations, but reveal lower values compared to the second group (Table 2);

(ii) The second group of samples SP$_2$, SP$_4$, SP$_5$, SP$_6$, SP$_7$, and SP$_8$ includes values over 2.5 mg l^{-1} that are not in accordance with EU and WHO regulations (Table 1).

3.17 Results for ammonia (NH$_3^-$)

Ammonia (NH$_3^-$) is a very important parameter to define in waters or sewage because amounts exceeding the limits should raise great concern. In SP$_1$ of the Mirusha River basin, NH$_3^-$ value was 0.09 mg l^{-1} and in SP$_4$ of the Stanishor River basin, it was 0.03 mg l^{-1}, whereas in other samples it was immeasurable because it was outside the metering range or spectrophotometric determinant. The lowest and the highest values of NH$_3^-$ are divided into two groups:

(i) The first group that includes SP$_4$ of the Stanishor River is in accordance with EU and WHO regulations (Table 1).

(ii) The second group, all samples including SP$_1$, SP$_2$, SP$_3$, SP5, SP$_6$, and SP$_7$ are not in accordance with EU and WHO regulations (Tables 1 and 2).

4 Conclusion

Based on the results, the studied river waters are heavily contaminated with nitrites, ammonium ions, phosphate ions, and BOD5. The water pollution of these rivers, as mentioned above, is caused by discharges from households, the food industry, and the application of chemicals in agriculture. Concentrations beyond the reference values of these pollutants directly affects the flora and fauna of the river waters, and thus are fatal for aquatic life. The primary goal of every state, and of Kosovo, is to protect the quality of water, and precisely for this reason, the state institutions, both at local and central level, should not only be committed to the permanent monitoring of these river waters, but should also construct an implant structure, where the Mirusha and Stanishor rivers merge with the waters of Morava River.

Discussion of the results and comparison of different parameters of SP$_1$–SP$_8$ samples was very important in order to gain insight into how the parameters deviate. According to our research, the main problem of deviation was the purification of industrial pipes with the CIP system, since all the waters containing a large number of microorganisms are released into these rivers, resulting in extreme pollution due to the lack of wastewater treatment plants in the processing industry.

List of abbreviations
Popis kratica

BOD5	– 5-day biochemical oxygen demand – petodnevna biokemijska potrošnja kisika
CIP	– Clean-in-place – CIP čišćenje
COD	– chemical oxygen demand – kemijska potrošnja kisika
CS	– carbonic strength – ugljična čvrstoća
CW	– conductivity of water – vodljivost vode
DO	– dissolved oxygen – otopljeni kisik
EDTA	– ethylenediaminetetraacetic acid – etilendiamintetraoctena kiselina
GH	– general hardness – ukupna tvrdoća
ISO	– International Organization for Standardization – Međunarodna organizacija za standardizaciju
NTU	– nephelometric turbidity unit – nefelometarska jedinica mutnoće
SP	– sample – uzorak

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SAŽETAK

Utjecaj urbanizacije i industrije na onečišćenje rijeka općine Gjilan, Kosovo

Valdrin M. Beluli

Grad Gjilan (42°28′08″, V 21°27′48″ L) jedan je od sedam najvećih gradova na Kosovu. Kroz njega prolaze tri rijeke: Mirusha i Stanishor koje se miješaju i ulijevaju u najveću rijeku Moravu. Razlog za istraživanje tih rijeka je njihovo onečišćenje nastalo ispuštanjem industrijskih voda. Analiza tih rijeka pokazuje izrazito onečišćenje te neusklađenost nekih fizikalno-kemijskih parametara s propisima Europske unije (EU) i Svjetske zdravstvene organizacije (SZO). Analizirani su sljedeći parametri: pH, CW, NTU, DO, COD, BOD5, A-HCl, HCO_3, GH, CS, Cl^-, Cl_2, Ca^{2+}, Mg^{2+}, NO_2^-, NO_3^-, PO_4^{3-} i NH_3^-.

Ključne riječi
Rijeke, industrije, izrazito onečišćenje, fizikalno-kemijski parametri, EU, SZO

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